

This is the final peer-reviewed accepted manuscript of:

*Scherer G.W., Sassoni E., Mineral Consolidants, In: Rörig-Dalgaard I. & Ioannou I. (Eds) Proceedings of the International RILEM Conference Materials, Systems and Structures in Civil Engineering 2016 - Segment on Historical Masonry, Lyngby (DK), 22-24 August 2016, p. 1-10, ISBN: 978-2-35158-178-0*

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## **MINERAL CONSOLIDANTS**

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### **Abstract**

Inorganic consolidants, such as ethyl silicate, nanolime and ammonium oxalate, have proven to be effective for certain materials, but each has its drawbacks. This has recently led to the investigation of hydroxyapatite (HAP) as a novel inorganic consolidant, which demonstrated excellent performance on carbonate stones. Considering that a mineral that matched calcite crystal lattice parameters even more closely than HAP would be expected to provide a consolidating action even greater than HAP, in this study aluminum phosphate (AP) was investigated as a potential new consolidant. Indeed, AP has lattice parameters differing from those of calcite by only 1%. The consolidating ability of AP was preliminarily investigated here in comparison with HAP. Both treatments were tested on artificially weathered marble samples, in the view of their application for conservation of sugaring marble. A novel method is also proposed for producing samples with near-surface damage similar to that of sugaring marble in the field. The results of the study point out that the novel weathering method is able to provide samples with tailored gradient in dynamic elastic modulus, closely resembling naturally sugaring marble. The AP treatment was found to significantly improve the dynamic elastic modulus of weathered marble, at least as efficiently as the HAP treatment investigated in this study. This confirmed the high potential of AP as a new inorganic consolidant.

### **1. Introduction**

Consolidation is often needed to restore mechanical properties of stones used in historic masonry and decorative architectural elements, which undergo deterioration because of chemical-physical processes (such as freezing-thawing cycles, salt crystallization, swelling of clays). Organic consolidants, such as acrylic and epoxy resins, were widely used in the past, because of their good adhesive properties and strengthening ability. However, their behavior over time has proven to be substantially unsatisfactory, because of their tendency to change color, their sensitivity to UV light and their generally low durability [1]. Consequently, research has recently mainly focused on inorganic consolidants.

Silicate consolidants, such as TEOS-based products, have a good ability to strengthen silicate substrates (sandstones, but also fired clay bricks) [2-4]. Thanks to the chemical bonding between the silica gel formed by TEOS hydrolysis and condensation and the hydroxyl groups present on the surface of silicate substrates, a remarkable increase in mechanical properties can be achieved after consolidation. However, the efficacy of TEOS-based consolidants is significantly lower in the case of carbonate stones, such as porous limestone and marble (widely used for masonry blocks and decorative elements, respectively). As carbonate stones lack hydroxyl groups on their surface, only physical-mechanical interlocking can take place between the consolidant and the substrate, which results in limited consolidating efficacy [2,3]. A further limitation of silicate consolidants, independent of the substrate, is that TEOS hydrolysis-condensation reactions take a long time to be completed (even more than 6 months) [3]. As a consequence, the treated stone remains hydrophobic for a long time, which can be undesirable in case water-based treatments need to be applied after consolidation or in case water is trapped behind the hydrophobic layer. To accelerate TEOS hydrolysis-condensation reactions, innovative methods have recently been proposed, based on stone treatment with water or water-ethanol mixtures to favor substitution of ethoxy groups with hydroxyl groups [5,6].

In the case of carbonate stones, a potentially highly compatible consolidant is lime, which turns into calcium carbonate upon carbonation. To overcome the limitations of traditional lime-based treatments, such as impregnation with limewater and lime-milk (viz., low solubility of lime in water, need of repeated applications, slow carbonation process, low penetration depth), nanolimes have recently been proposed [7]. Thanks to their nanometric size, the carbonation process is faster and the penetration depth is expected to be higher. Nonetheless, since lime nanoparticles tend to agglomerate, particles accumulate near the surface and consequent whitening of the treated stone is frequent. To improve these aspects, several strategies are currently under investigation, such as tuning of the solvent used for particle dispersion [8].

An alternative treatment for consolidation of carbonate stones is that based on calcium oxalate formation. By treating stone with an aqueous solution of ammonium oxalate, calcium oxalate is formed by reaction with the calcitic substrate. The treatment, originally proposed for wall painting conservation [9], has been found to provide a good protective action to marble surfaces [10]. The formation of a coherent and non-porous layer of calcium oxalate over calcite is indeed able to increase stone resistance to dissolution in rain; however, the solubility of calcium oxalate is similar to that of calcite, so its long-term benefits are not yet clear. The treatment has proven to offer only a minor improvement in mechanical properties of treated marble, likely because of the limited depth of calcium oxalate formation [11].

Taking inspiration from the calcium oxalate treatment, in 2011 we proposed a novel consolidant for carbonate stones, based on formation of hydroxyapatite (HAP,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}_2)$ ) [12]. HAP is formed by treating the calcitic substrate with an aqueous solution of diammonium hydrogen phosphate (DAP). With respect to the calcium oxalate, HAP has the advantage of having a much closer match with calcite in terms of lattice parameters and a much lower solubility and dissolution rate [12,13] (Table 1). The match between lattice parameters is important because, if a layer of HAP can be grown epitaxially

over calcite, a very efficient bonding can be expected, resulting in very efficient consolidating and protecting abilities. Very encouraging results have been obtained so far on the use of HAP for consolidation of marble and limestone [11,12,15,16] and on marble protection from dissolution in rain [10,17]. However, while the 5% lattice mismatch might be small enough to favor nucleation of HAP on calcite, it is large enough to result in considerable stress if the layer grows more than a few nm thick. That may explain why the HAP deposits are not dense layers, but instead are flowery and porous [18].

To overcome the limitation deriving from the 5% mismatch between HAP and calcite lattice parameters, a different mineral would be needed, exhibiting an even closer match with calcite. As reported in Table 1, aluminum phosphate (AP,  $\text{AlPO}_4$ , the mineral berlinite) has lattice parameters differing by only 1% from those of calcite. Based on data from the literature [19,20,21], we estimate the solubility product of AP to be about  $5.7 \times 10^{-22}$ , which is much lower than that of calcite ( $3 \times 10^{-9}$ ). Therefore, AP has the potential of forming a strongly bonded and insoluble layer over calcite grains, thus providing protection against dissolution as well as mechanical strengthening. In this paper, we present some preliminary results on the consolidating ability of AP, in comparison with HAP. Both treatments were tested on marble samples artificially weathered to simulate sugaring marble.

Sugaring is a deterioration phenomenon that frequently affects marble, both in ancient and modern buildings [11,22]. As calcite deforms anisotropically upon heating, repeated day/night temperature excursions cause stress and micro-cracking at the boundaries between calcite grains, resulting in grain detachment and loss [23]. Sugaring mainly affects the outer surface, which is directly exposed to solar radiation and to air temperature variations, while the underlying substrate is usually undamaged. Since testing of marble consolidants requires the use of samples with physical-mechanical properties as similar as possible to those of deteriorated marble in the field [11], we have developed a new method for reproducing the near-surface damage found in sugaring marble, starting from freshly quarried marble.

Therefore, in the present paper the new method for producing artificially weathered marble samples is presented first and then some preliminary results are reported and discussed on the use of HAP and AP to consolidate weathered marble.

Table 1. Lattice parameters and solubility products of calcite, ammonium oxalate, hydroxyapatite (HAP) and aluminum phosphate (AP). Data are taken from [13] for calcite, ammonium oxalate and HAP. Lattice parameters of AP are taken from [14].

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$K_{sp}$ (25°C)
Calcite (2×)	9.98	9.98	33.82	$3 \times 10^{-9}$
Calcium oxalate (2×)	12.58	29.16	20.32	$2 \times 10^{-9}$
HAP	9.43	9.43	6.88	$3 \times 10^{-59}$
AP (2×)	9.88	9.88	21.89	$6 \times 10^{-22}$

## 2. Materials and methods

### 2.1 Marble accelerated weathering

Carrara marble (provided by BasketweaveMosaics.com, USA) was used for the tests. Cubes with 5 cm edge length were wet sawn from a freshly quarried slab. To simulate the near-surface damage of sugaring marble, the core idea is to induce a gradient in marble mechanical properties by putting samples in contact with a hot plate for a certain time. In this way, the part of the sample in contact with the hot plate undergoes micro-cracking at the boundaries between grains, whereas at a certain distance from the plate marble remains unheated and hence undamaged.

To define what should be the depth to which marble should be weathered, real samples of sugaring marble from the field were considered. In real samples, sugaring was found to affect marble to a depth of about 1 cm from the surface. In this 1 cm-deep surface layer, marble ultrasonic pulse velocity (UPV, often used to characterize the conservation state of marble) was found to be reduced by about 20% with respect to the undamaged substrate [11]. Consequently, we adopted a decrease in UPV of 20% in the first centimeter from the surface as the target of our artificial weathering procedure.

To define what temperature and what heating duration should be used to produce the desired weathering level, we first correlated the heating temperature with the UPV, by heating samples at 100, 200, 300 and 400 °C for 1 hour and measuring the corresponding decrease in UPV. Having determined that the desired UPV decrease is reached by heating at 100 °C (as detailed in a future publication), the time of heating necessary to induce the UPV decrease in the first centimeter from the surface, but not in the underlying part, was calculated as follows.

Holes with increasing length were drilled in a marble cube as illustrated in Figure 1. Thermocouples were inserted into the holes to allow temperature measurement at increasing distance from the heating plate (nominally, 0, 10, 20, 30, 40 and 50 mm). The cube was put over the heating plate, initially cold, and the sides and the top were insulated using a high temperature-resistant insulator, to ensure that the heat flux was one-dimensional. The heating plate was then turned on and the temperature progressively increased up to 400 °C. Temperature variations at different distances from the plate were then measured as a function of time. In the described conditions, the equation governing the heat flow is:

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( k(x, t) \frac{\partial T}{\partial x} \right) \quad (1)$$

where  $T$  is the temperature,  $t$  is the time,  $x$  is the distance from the heating plate and  $k$  is marble thermal diffusivity. We assumed the same exponential decrease of  $k$  observed in Holston marble by Hanley et al. [24]. By fitting temperature values measured at different distances from the plate to a numerical solution of Eq. (1), it was possible to calculate  $k$ , which was found to vary from  $\sim 1 \times 10^{-6} \text{ m}^2/\text{s}$  at room temperature to  $\sim 5 \times 10^{-7} \text{ m}^2/\text{s}$  at 300 °C. For this variation of  $k$  with temperature, it was calculated that putting the sample in contact with the heating plate at 200 °C for 20 seconds would cause an average decrease in dynamic

elastic modulus ( $E_d$ , related to UPV through the density) in the first centimeter from the surface very similar to that exhibited by naturally weathered marble. The details of the model used to calculate the heating temperature and time will be presented in a future publication. The model can be used to simulate arbitrary heating procedures.

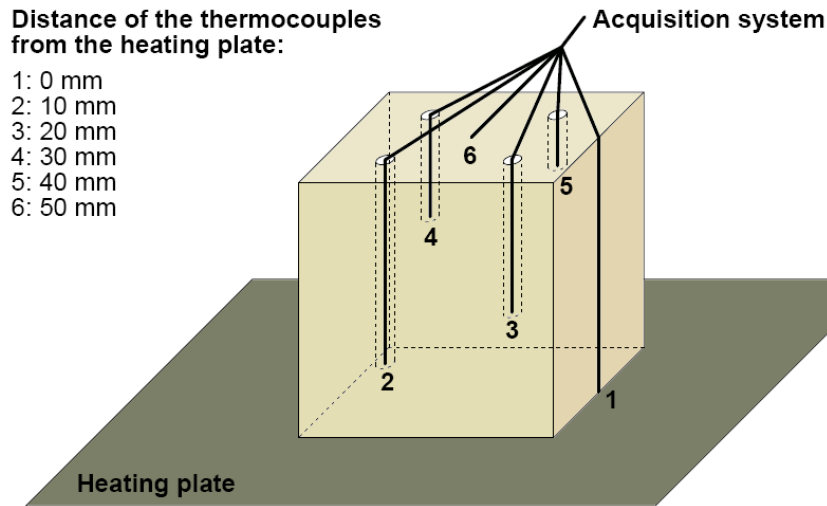


Figure 1. Scheme illustrating sample instrumentation. During the heating experiment, the marble sample was surrounded by a high temperature-resistant thermal insulator.

To verify the model predictions, a 5 cm edge cube, instrumented as illustrated in Figure 1 and surrounded by a high temperature-resistant insulator, was placed over an heating plate originally at 200 °C for 20 seconds. After cooling, the UPV was measured at the two extremities of the sample (i.e. in the parts distant 0-1 cm and 4-5 cm from the heated surface). The UPV was measured by the transmission method, using a PUNDIT commercial instrument with 54 kHz transducers and a rubber couplant between the sample and the transducers. From UPV,  $E_d$  was calculated as  $E_d = \rho \times \text{UPV}^2$ , where  $\rho$  is sample density.  $E_d$  values measured before and after heating were then compared.

## 2.2 Marble treatment

For the HAP treatment, an aqueous solution containing 0.1 M DAP, 0.1 mM  $\text{CaCl}_2 \cdot 10\text{H}_2\text{O}$  and 10 vol% ethanol, was used. Ethanol was added in view of its beneficial effect in promoting HAP formation, as recently reported in [17]. For the AP treatment, samples were treated with a 0.1 M DAP and 0.1 mM  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  aqueous solution, also containing 10 vol% ethanol. Ethanol was added because preliminary tests revealed that it resulted in a reduction in cracking of the film formed after treatment. Both the HAP and AP treatments were performed by submerging marble samples ( $5 \times 5 \times 1 \text{ cm}^3$ ) in 200 mL of the consolidating solutions for 24 hours. The samples were then rinsed with deionized water and dried at room temperature.

The morphology and the elemental composition of the new phases formed after treatment were analyzed by scanning electron microscope (FEG-SEM XL30 Philips), equipped with an

energy dispersive x-ray spectroscopy device (Oxford Instruments EDS probe). SEM-EDS analysis was carried out on previously undamaged marble samples.

The consolidating efficacy was evaluated on thermally weathered samples. Because the weathering method described in § 2.1 was still under development when the consolidating efficacy of AP was investigated, tests on HAP and AP were carried out on samples pre-weathered following a different method that we previously developed [12,25]. Samples were heated in an oven for 1 hour, some of the samples at 100 °C and some at 400 °C. In this way, it was possible to obtain uniformly damaged samples, having different levels of micro-cracking (more diffused micro-cracking in samples heated at 400 °C). To favor the penetration of the consolidating solutions into samples pre-heated at 100 °C, these samples were vacuum impregnated. The consolidating ability of the two treatments was evaluated by comparing UPV and  $E_d$  before and after consolidation, determined as described in § 2.1.

### **3. Results and Discussion**

#### **3.1 Marble accelerated weathering**

To verify what the mathematical model predicted (i.e. an average 20% decrease in UPV in the first centimeter of the sample put in contact with the heating plate at 200 °C for 20 seconds), these conditions were reproduced experimentally and the UPV variation measured in different parts of the sample. Although the heating plate was originally at 200 °C, upon contact with the sample the temperature rapidly decreased, so that after 20 seconds of contact the surface temperature reached 140 °C. For heating at 140 °C, the  $E_d$  reduction is expected to be about -50% (based on the correlation between temperature and  $E_d$  variation, that will be presented in a future publication). As the surface was heated at 140 °C and, at a distance of 1 cm from the surface, the temperature was still basically unchanged (maximum temperature 39 °C), the average variation in  $E_d$  in the first centimeter from the plate was expected to be about -25%.

The UPV measurements after the heating experiment provided a good confirmation of the expected results. Indeed, while the part of the sample between 4 and 5 cm from the heated surface exhibited no  $E_d$  variation, the first centimeter in contact with the plate exhibited an  $E_d$  decrease of -29%, in good agreement with what was expected. A more continuous profiling of the damage induced by heating on the plate can be provided by nanoindentation tests, carried out at increasing distance from the heated surface. These tests are currently in progress.

#### **3.2 Marble treatment**

The morphology and the elemental composition of the new phases formed after treatment are illustrated in Figure 2, where untreated marble is also reported for comparison's sake. After the HAP treatment, the marble surface uniformly exhibits a new flowery morphology, typically ascribed to HAP. Accordingly, the EDS spectrum reveals the presence of P, alongside Ca and O. The coating appears as continuous, without uncovered areas, and uncracked. This can be ascribed to the beneficial effect of ethanol on HAP crystallization [17]. In fact, for the same DAP and  $\text{CaCl}_2 \cdot 10\text{H}_2\text{O}$  concentrations, but without ethanol addition, uncoated areas remain and microcracks are present in the film.

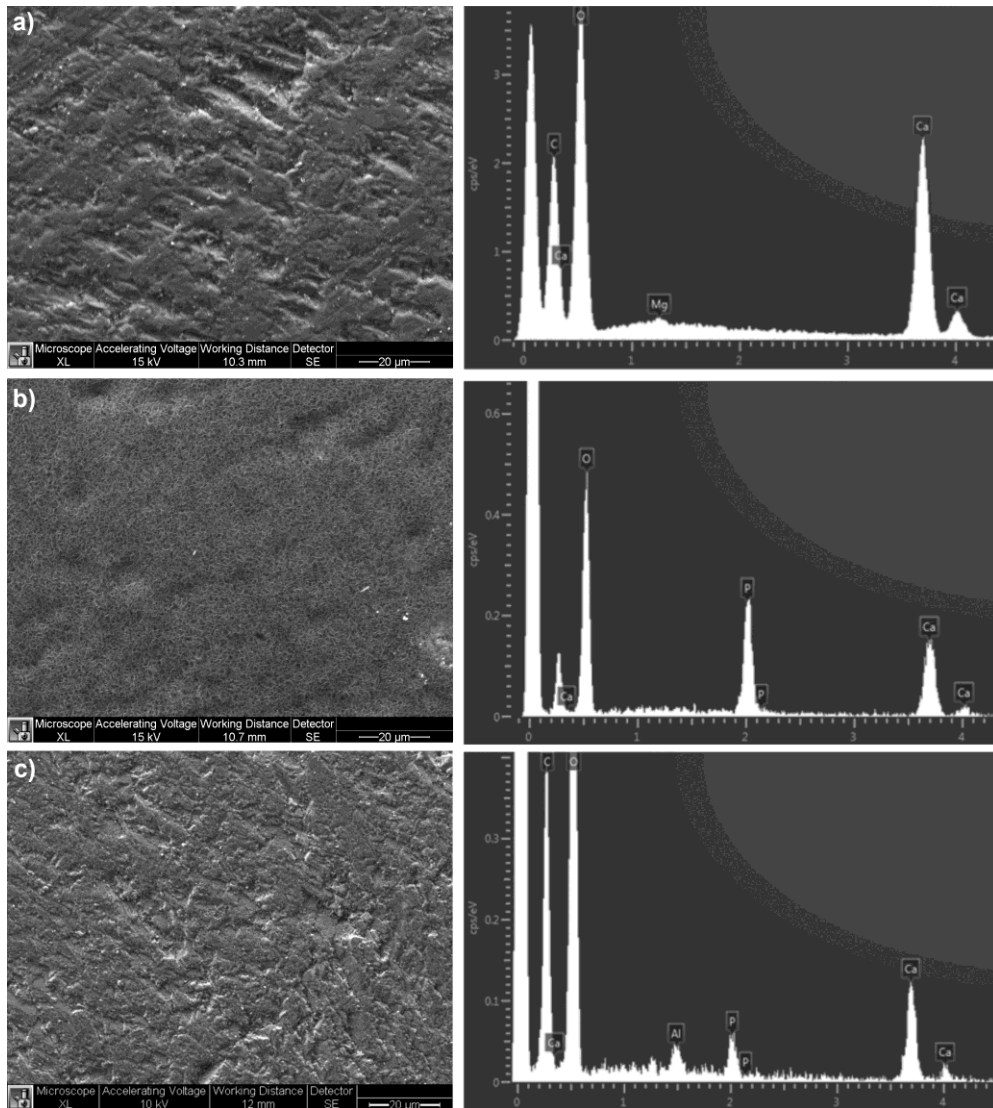


Figure 2. SEM images (magnification 1000 $\times$ ) and respective EDS spectra of untreated marble (a) and marble treated with HAP (b) and AP (c).

In the case of the AP treatment, no apparent alteration of the original marble morphology is visible (Figure 2c). Nonetheless, EDS spectra acquired in different positions reveal well defined peaks of Al and P. As these peaks are clearly visible even after sample rinsing with water at the end of the 24 hour treatment, the formation of a new phase is suggested (if Al and P were owing to some compound simply deposited over marble surface, they would be washed away by rinsing). Notably, the Al/P weight ratio acquired in different positions ranges from 0.43 to 0.54, hence it is close to the 0.87 Al/P weight ratio of stoichiometric  $\text{AlPO}_4$ . This is important, considering that in the consolidating solution the DAP concentration was 1000 times higher than that of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.1 M and 0.1 mM, respectively). This further suggests that a new phase, with a composition fairly close to that of  $\text{AlPO}_4$ , was formed after the treatment.



In terms of consolidating ability, the  $E_d$  variations after heating and after consolidation are illustrated in Figure 3. As expected, heating at 400 °C caused significant additional damage compared to heating at 100 °C (average  $E_d$  decreases of -94% and -32%, respectively).

In the case of HAP,  $E_d$  increases of +18% and +143% were found after consolidation for samples pre-heated at 100 and 400 °C, respectively (Figure 3). This trend in consolidating ability (higher percentage increase in  $E_d$  for more decayed samples) is consistent with previously obtained results on limestone consolidation by HAP [12]. Although the  $E_d$  increases were remarkable, still the initial  $E_d$  was not fully restored after consolidation. In previous studies on consolidation of sugaring marble by HAP, full recovery of the original  $E_d$  was achieved [11,26]. The different results obtained in the present study are thought to derive from the different formulation tested here: whereas in the cited studies full  $E_d$  recovery was obtained by using a higher DAP concentration [11] or a double DAP solution applications [26], in the present study a single application of a diluted DAP solution was performed.

In the case of the AP treatment,  $E_d$  increases of +24% and +280% were found for samples pre-heated at 100 °C and 400 °C, respectively (Figure 3). Similarly to the case of HAP, the AP treatment exhibited the highest strengthening ability on the highly damaged substrate, even if full recovery of the initial  $E_d$  was not achieved. Based on these results, the AP treatment exhibits a consolidating ability superior to that of the HAP treatment, at least in the case of the HAP formulation tested in this study. The AP treatment is hence confirmed as highly promising and future optimization (in terms of aluminum and phosphate precursors, addition of chelating agents to increase the precursors concentration, pH control, etc.) is expected to significantly improve its consolidating ability.

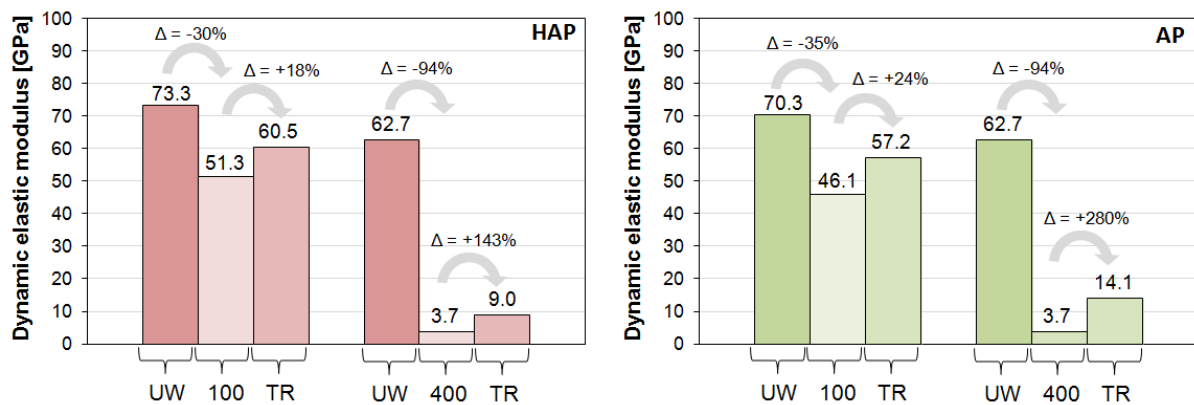


Figure 3.  $E_d$  variations after damaging and consolidation by HAP (left) and AP (right) (UW = unweathered; 100 = weathered at 100 °C; 400 = weathered at 400 °C; TR = treated).

#### 4. Conclusions

In this study, we presented a novel method for producing artificially decayed samples with properties resembling those of naturally sugaring marble and we reported the first results on the use of aluminum phosphate for consolidation of weathered marble.

The new artificial weathering method is based on production of near-surface damage in marble samples by contact with a hot plate at a certain temperature and for a certain time,

which can be calculated by a mathematical model. The method proved to be capable of providing samples with a gradient in ultrasonic pulse velocity and dynamic elastic modulus that closely matches that of naturally weathered marble. In the future, the mathematical model can be used for simulating arbitrary heating procedures.

The aluminum phosphate treatment was found to cause a significant increase in the dynamic elastic modulus of weathered marble, the consolidating efficacy varying as a function of the initial level of damage in marble. The aluminum phosphate treatment was found to be more effective than the hydroxyapatite treatment, tested here in a new formulation for the first time. The potential of the new aluminum phosphate treatment is hence confirmed as very high and a further improvement of its consolidating ability is expected in the future from treatment optimization (in terms of aluminum and phosphate precursors, addition of chelating agents to increase the precursors concentration, pH control, etc.).

### Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 655239 (HAP4MARBLE project, "Multi-functionalization of hydroxyapatite for restoration and preventive conservation of marble artworks").

### References

- [1] Skoulikidis, T., Vassiliou, P., Tsakona, K., Surface consolidation of Pentelic marble - Criteria for the selection of methods and materials - The Acropolis case, *Environ Sci & Pollut Res* 12 (2005), 28-33
- [2] Wheeler, G.S., Alkoxysilanes and the Consolidation of Stone (Research in conservation), The Getty Conservation Institute, Los Angeles, 2005
- [3] Scherer, G.W. and Wheeler G.S., Silicate consolidants for stone, *Key Engineering Materials* 391 (2009), 1-25
- [4] Graziani, G., Sassoni, E., Franzoni, E., Experimental study on the salt weathering resistance of fired clay bricks consolidated by ethyl silicate, *Materials and Structures*, DOI 10.1617/s11527-015-0665-8
- [5] Naidu, S., Liu, C., Scherer, G.W., New techniques in limestone consolidation: Hydroxyapatite-based consolidant and the acceleration of hydrolysis of silicate-based consolidants, *J Cult Herit* 16 (2015), 94-101
- [6] Franzoni, E., Graziani, G., Sassoni, E., TEOS-based treatments for stone consolidation: acceleration of hydrolysis-condensation reactions by poulticing, *Journal of Sol-Gel Science and Technology* 74 (2015), 398-405
- [7] Daniele, V., Taglieri, G., Quaresima, R., The nanolimes in Cultural Heritage conservation: Characterization and analysis of the carbonatation process, *J Cult Herit* 9 (2008), 294-301
- [8] Borsoi, G., Lubelli, B., van Hees, R., et al., Effect of solvent on nanolime transport within limestone: how to improve in-depth deposition, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, DOI: <http://dx.doi.org/doi:10.1016/j.colsurfa.2016.03.007>
- [9] Matteini, M., Moles, A., S. Giovannoni, Calcium oxalate as a protective mineral system for wall paintings: methodology and analyses, *III Int. Symp. Conservation of Monuments in the Mediterranean Basin*, ed. Fassina, V., Ott, H., Zezza, F., 1994
- [10] Naidu, S., Blair, J., Scherer, G.W., Acid-Resistant Coatings on Marble (submitted)

- [11] Sassoni, E., Graziani, G., Franzoni, E., Repair of sugaring marble by ammonium phosphate: comparison with ethyl silicate and ammonium oxalate and pilot application to historic artifact, *Materials and Design* 88 (2015) 1145-1157
- [12] Sassoni, E., Naidu, S., Scherer, G.W., The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones, *J Cult Herit*, 12 (2011) 346-355
- [13] Naidu, S., Sassoni, E., Scherer, G.W., New treatment for corrosion-resistant coatings for marble and consolidation of limestone, in Stefanaggi, M., Vergès-Belmin, V. (Eds), "Jardins de Pierres – Conservation of stone in Parks, Gardens and Cemeteries", Paris (F) 22-24 June 2011, 289-294
- [14] [http://database.iem.ac.ru/mincryst/s\\_full.php](http://database.iem.ac.ru/mincryst/s_full.php)
- [15] Sassoni, E., Graziani, G., Franzoni, E., An innovative phosphate-based consolidant for limestone. Part 1: Effectiveness and compatibility in comparison with ethyl silicate, *Construction and Building Materials*, 102 (2016) 918-930
- [16] Sassoni, E., Graziani, G., Franzoni, E., An innovative phosphate-based consolidant for limestone. Part 2: Durability in comparison with ethyl silicate, *Construction and Building Materials*, 102 (2016) 931-942
- [17] Graziani, G., Sassoni, E., Franzoni, E., Scherer, G.W., Hydroxyapatite coatings for marble protection: Optimization of calcite covering and acid resistance, *Applied Surface Science* 368 (2016), 241-257
- [18] Naidu, S., Scherer, G.W., Nucleation, growth and evolution of calcium phosphate films on calcite, *Journal of Colloid and Interface Science* 435 (2014): 128-137
- [19] Arun S. Wagh and Seung Y. Jeong, "Chemically Bonded Phosphate Ceramics: I, A Dissolution Model of Formation", *J. Am. Ceram. Soc.*, 86 [11] (2003) 1838-[Dash]44
- [20] F.J. Peryea and J.A. Kittrick, "Relative solubility of corundum, gibbsite, boehmite, and diaspore at standard state conditions", *Clays and Clay Minerals*, 36 [5] (1988) 391-396
- [21] Wolfgang Hummel, Urs Berner, Enzo Curti, F.J. Pearson, Tres Thoenen, "Nagra/PSI Chemical Thermodynamic Data Base 01/01", (Universal-Publishers, uPUBLISH.com, USA, 2002) pp. 589 ISBN-10: 1581126204, ISBN-13: 978158112620
- [22] Sassoni E., Franzoni E., Sugaring marble in the Monumental Cemetery in Bologna (Italy): characterization of naturally and artificially weathered samples and first results of consolidation by hydroxyapatite, *Applied Physics A: Materials Science & Processing*, 117 (2014) 1893-1906
- [23] Siegesmund, S., Ullemeyer, K., Weiss, T., Tschegg, E.K., Physical weathering of marbles caused by anisotropic thermal expansion, *Int J Earth Sci*, 89 (2000) 170-182
- [24] Hanley, E.J., Dewitt, D.P., Roy, R.F., The thermal diffusivity of eight well-characterized rocks for the temperature range 300-1000 K, *Engineering Geology*, 12 (1978), 31-47
- [25] Franzoni, E., Sassoni, E., Scherer, G.W., Naidu, S., Artificial weathering of stone by heating, *Journal of Cultural Heritage*, 14S (2013) e85-e93
- [26] Sassoni, E., Graziani, G., Franzoni, E., Scherer, G.W., Consolidation of sugaring marble by hydroxyapatite: some recent developments on producing and treating decayed samples, *Proc. of 13<sup>th</sup> International Congress on the Deterioration and Conservation of Stone*, Paisley (UK) 6th-10th September 2016 (submitted)